

EFFECT OF PRE-TREATMENT ON METHANOL SYNTHESIS FROM CO₂/H₂ OVER Cu/ZnO/Al₂O₃

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INTRODUCTION

Methanol synthesis from CO₂ and H₂ has recently received much attention as one of the promising processes to convert CO₂ into raw materials for fuel and chemicals. Copper-based catalysts are highly effective for this reaction, and a number of studies have been done to understand the mechanisms of catalytic action. Chinchin et al.^{1,2} have reported that methanol synthesis occurs exclusively on the surface of metallic copper and the activity is directly proportional to this copper surface area. They attributed no special role to the support other than to maintain the dispersion of copper on the catalyst surface. Evidence that Cu⁺ is the pivotal catalytic species, however, has been presented by Sheffer and King^{3,4} who found that the activity for methanol synthesis from CO over unsupported copper catalysts increases with the concentration of Cu⁺ sites stabilised by alkali compounds. More recent studies by Fujitani et al.^{5,6} have demonstrated the existence of an optimal level of oxygen coverage for methanol activity, although this was done for copper catalysts supported a very wide range of oxide materials. They found that the activity increased linearly with the oxygen coverage below $\Theta_o = 0.16$, and then decreased above $\Theta_o = 0.18$, suggesting that the active component is some combination of Cu⁺ and Cu⁰, where the ratio of Cu⁺/Cu⁰ controlled the specific activity.

The present paper reports the effect of CO₂/CO pre-treatment on methanol synthesis from CO₂/H₂ over Cu/ZnO/Al₂O₃ catalysts. Instead of using widely varying oxide materials, oxygen coverage is varied in the pre-treatment on a single well-studied catalyst via the gas phase, where the CO₂/CO ratio has been demonstrated to have a linear correlation with the oxygen coverage under reaction conditions¹. Possible contributions from changes in surface state are explored by measuring the response of methanol rate to these conditions.

EXPERIMENTAL

The Cu/ZnO/Al₂O₃ catalyst were prepared by precipitation of the respective metal nitrates using Na₂CO₃ as the precipitating agent. The precipitate was washed with distilled water until analysis showed the presence of Na was no greater than 1-2 ppm. The dried precipitate was then calcined in air at 300 °C for 6 h. After the addition of 2% (w/w) graphite for binding purposes, pellets of 2 g cm⁻³ density were formed. These were crushed and sieved to a particle size range of 106-250 µm. Elemental analysis using x-ray fluorescence revealed the composition of the catalyst to be 61.0% CuO, 27.5% ZnO, and 11.5% Al₂O₃.

The reactor system used for the activity studies consisted of a continuous tubular flow fixed-bed microreactor which was operated at 4.5 MPa and 215 °C. The synthesis gas composition was a 1:4 CO₂/H₂ mixture fed through to the reactor via Brooks high pressure mass flow controllers. On-line gas analysis was accomplished using a GC-MS system. An isothermal sampling valve injects 0.5 ml samples from the heated effluent downstream of the reactor to a Perkin Elmer 8500 gas chromatograph. Separation and detection of products were performed by a Poropak Q column and a thermal conductivity detector, respectively. Downstream of the gas chromatograph sampling valve, the gas was analysed using a Leda-Mass quadrupole mass spectrometer with a Spectra Microvision analyser unit.

Prior to reaction, the catalysts were activated *in situ* by reduction of the CuO component to metallic copper. Under flowing 5% H₂ in He the temperature was increased by 2 °C min⁻¹ to 215 °C and held for 12 h. After the initial reduction, the reactor is flushed with He and the pre-treatment gas mixture of CO₂ and CO introduced. These conditions are maintained for 1 h before the reactor is again flushed with He and pressurised to 4.5 MPa. At pressure, the synthesis gas mixture of 20% (v/v) CO₂ in H₂ is introduced, and the pressure maintained at 4.5 MPa. Rate

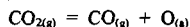
measurements were taken in a flow regime which obeys differential kinetics. Under these conditions, the rate is independent of the flow. This results in extremely low levels of conversion (generally less than 1%) such that the catalysts are essentially exposed only to reactants, and the rate reflects the intrinsic forward rate of reaction.

RESULTS AND DISCUSSION

In the absence of H_2 , no methanol is produced. Reaction was carried out under a lower temperature of 215 °C which is the temperature under which the catalyst charge is reduced with a stream of 5% hydrogen in helium. Whereas methanol synthesis is normally carried out at 250 °C, these isothermal conditions were chosen to minimise the time required to switch between the CO_2/CO pre-treatment and reaction under CO_2/H_2 .

At these temperatures, the initial rate of methanol synthesis from CO_2/H_2 (over the $Cu/ZnO/Al_2O_3$ catalyst reduced overnight with 5% hydrogen in helium but without further CO_2/CO pre-treatment) of about $0.045 \text{ mol h}^{-1} \text{ g}_{cat}^{-1}$ is substantially lower than those under industrial reactions conditions (about $0.20 \text{ mol h}^{-1} \text{ g}_{cat}^{-1}$ at 250 °C). Nevertheless, it is possible to observe the sensitivity of CO_2 hydrogenation to pre-treatment conditions of varying carbon dioxide concentrations as defined by R , where $R = CO_2/(CO_2 + CO)$, as described by Figure 1. Upon pre-treating with a stream of pure carbon monoxide ($R = 0$), hydrogenation of carbon dioxide yields methanol at a rate of about $0.045 \text{ mol h}^{-1} \text{ g}_{cat}^{-1}$, which is identical to that found in the case without CO_2/CO pre-treatment. This confirms that pre-treatment under carbon monoxide maintains the catalyst surface in a completely reduced state. As small amounts of carbon dioxide is introduced into the pre-treatment, however, the specific methanol rate begins to increase. This behaviour continues as R is increased until a maximum rate is reached at an R value between 0.7 and 0.8. Further increases in pre-treatment carbon dioxide concentration beyond this point brings about a decrease in the rate of methanol synthesis. In the extreme case, pre-treatment under pure carbon dioxide for 1 hour leads to a methanol rate of $0.055 \text{ mol h}^{-1} \text{ g}_{cat}^{-1}$.

The existence of an optimal CO_2/CO pre-treatment condition for methanol synthesis is significant as it supports the model where both Cu^0 and Cu^+ are important for the catalytic action. Interconversion between carbon dioxide and carbon monoxide takes place through a surface mediated process according to the equation



where $O_{(s)}$ is a surface oxygen species. The formation of $O_{(s)}$ by the dissociative adsorption of carbon dioxide was observed on $Cu(110)$ by Wachs and Madix⁷, and on polycrystalline copper, Cu/Al_2O_3 , and $Cu/ZnO/Al_2O_3$ by Chinchin and co-workers². As one measure of the state of a catalyst is its oxygen coverage, this is largely determined by the balance of carbon dioxide and carbon monoxide present in the gas phase. Thus, pre-treating the catalyst with the full range of R values between 0 and 1, permits the study of methanol synthesis in response to a wide range of surface conditions.

In order to assess the significance of this behaviour, a more detailed study into the transient kinetics is also necessary. Figure 2 shows the evolution of methanol production upon switching to synthesis conditions (20% carbon dioxide in hydrogen, 4.5 MPa, 215 °C) after the reactor was pressurised under helium. It can be seen that the response of the methanol signal is relatively fast, achieving a steady-state value after about 10 minutes time-on-stream. During the course of this transient, conditions on the surface are responding to the introduction of the new synthesis condition in the gas phase. Because this process occurs so quickly, faster in fact than the time scale at which quantitative measurements can be taken with the gas chromatograph, the methanol rates observed actually occur over a surface which has already achieved a dynamic equilibrium with the gas phase. Although it would seem that such a fast response of the surface would effectively erase the previously established pre-treatment conditions, this clearly does not happen. Furthermore, rather than drifting toward a common level of convergence, the different rates achieved under synthesis conditions possess a high degree of stability, without much appreciable change over the course of 24 hours. Therefore, that the rate does in fact depend on pre-treatment and that this rate remains stable over a long period of time imply the possible existence of rate multiplicity in some form.

One of the possible mechanisms by which a memory effect can take hold is via the support material. Work by Kanai et al.⁶ demonstrated the existence of a direct correlation between

increasing concentrations of ZnO_x species and increasing methanol activities. By reducing physical mixtures of Cu/SiO_2 and ZnO/SiO_2 at high temperatures, ZnO_x moieties migrate onto the surface of the copper particles creating a $\text{Cu}^+-\text{O}-\text{Zn}$ site and giving rise to the observed promotional effect. The presence of surface oxygen species could facilitate this interaction along the metal-support interfacial region, so that once the partially oxidised copper species are formed, they can be more readily stabilised by the ZnO along the periphery.

Non-linear behaviour is also known to occur in heterogeneous catalysis, especially of reactions on transition metals involving oxygen. A well known system which exhibits rate multiplicity is that of CO oxidation⁸. The existence of two distinct steady states in these systems is attributed to disparate activation energies for CO adsorption depending on surface morphology and oxygen coverage. While the role of surface oxygen has yet to be unequivocally established in methanol synthesis systems, there is evidence to suggest that it is similarly important in influencing the overall kinetics. One example reported by Chinchin et al.² shows that the presence of surface oxygen enhances both the adsorption of CO_2 as well as H_2 . It is possible, then, that this change to the adsorption activation energies of the reactant species brought about by surface oxygen can lead to multiple steady states.

CONCLUSIONS

The results show, therefore, that methanol synthesis from CO_2/H_2 is not most favoured over a highly reduced surface, but rather over one where both Cu^0 and Cu^+ are present. Despite the fast response of the surface to changes in the gas phase (i.e., in switching between the pre-treatment and synthesis conditions), there nevertheless seems to be a memory effect. The rate of methanol synthesis from CO_2/H_2 is dependent upon the pre-treatment with CO_2/CO mixtures, with an optimal pre-treatment corresponding to a CO_2 concentration of $R = 0.7$ to 0.8 . The different rates achieved after pre-treatment remain relatively stable up to 24 hours. This suggests that catalytic methanol synthesis systems operate in a non-linear fashion, perhaps mediated by surface oxygen and/or the oxide support.

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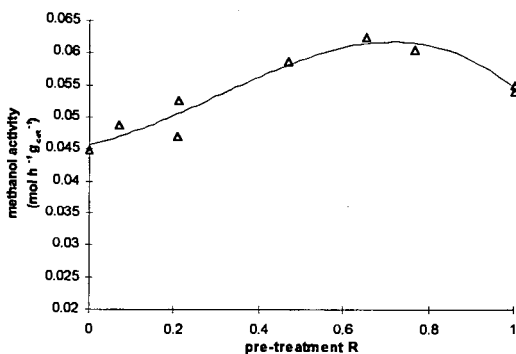


Figure 1. Methanol synthesis rate from CO_2/H_2 over $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ at 215 C and 4.5 MPa following CO_2/CO pre-treatment. $R = \text{CO}_2/(\text{CO}_2 + \text{CO})$.

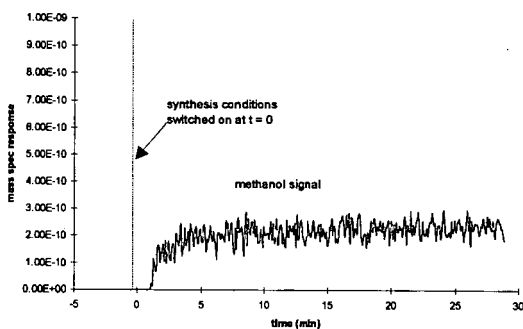


Figure 2. Transient response of methanol signal upon switching to synthesis conditions.